

Mass Balance, Steady-State Solution, and Response Time

Course overview: I introduce the primary organizing principle of water-quality modeling, the mass balance. It is used to derive a water-quality model for the response of a continuously stirred tank reactor, or CSTR. I develop and solve for a steady-state solution and present the notions of transfer functions and response times. I also derive the general time-variable solution of the mass balance model and calculate a response time to quantify temporal characteristics and the recovery of such systems.

Now that we have reviewed some fundamental concepts, let's tie them together and actually develop a water-quality model. Then we will solve the model to answer the two most commonly posed questions in water-quality modeling: If we institute a treatment program,

- How much will the water body improve?
- How long will it take for the improvement to occur?

3.1 MASS BALANCE FOR A WELL-MIXED LAKE

A completely mixed system, or *continuously stirred tank reactor (CSTR)*, is among the simplest systems that can be used to model a natural water body. It is appropriate for a receiving water in which the contents are sufficiently well mixed as to be uniformly distributed. Such a characterization is often used to model natural lakes and some impoundments.

A hypothetical completely mixed system is depicted in Fig. 3.1. Note that I have included a number of sources and sinks that are typically encountered when

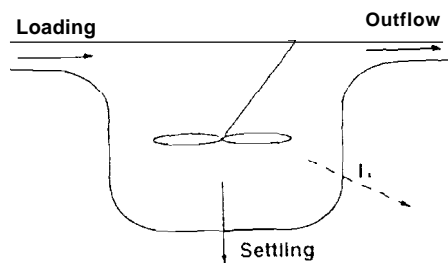


FIGURE 3.1
A mass balance for a well-mixed lake. The arrows represent the major sources and sinks of the pollutant. The dashed arrow for the reaction sink is meant to distinguish it from the other sources and sinks, which are transport mechanisms.

modeling water quality. For a finite time period the mass balance for the system can be expressed as

$$\text{Accumulation} = \text{loading} - \text{outflow} - \text{reaction} - \text{settling} \quad (3.1)$$

Thus there is a single source that contributes matter (loading) and three sinks that deplete matter (outflow, reaction, and settling) from the system. Note that other sources and sinks could have been included. For example volatilization losses (that is, transfer of the pollutant from the water to the atmosphere) could exit across the lake's surface. However, for simplicity, we limit ourselves to the sources and sinks depicted in Fig. 3.1.

Although Eq. 3.1 has descriptive value, it cannot be used to predict water quality. For this we must express each term as a function of measurable variables and parameters.

Accumulation. Accumulation represents the change of mass M in the system over time t :

$$\text{Accumulation} = \frac{\Delta M}{\Delta t} \quad (3.2)$$

Mass is related to concentration by (Eq. 1.1)

$$c = \frac{M}{V} \quad (3.3)$$

where V = volume of system (L^3). Equation 3.3 can be solved for

$$M = Vc \quad (3.4)$$

which can be substituted into Eq. 3.2 to give

$$\text{Accumulation} = \frac{\Delta Vc}{\Delta t} \quad (3.5)$$

In the present case we assume that the lake's volume is constant. This assumption allows us to bring the term V outside the difference:

¹Although this is a good assumption in many cases, it is not always true. For example many lakes and reservoirs in the United States are used for power production and water supply. Some of

$$\text{Accumulation} = V \frac{\Delta c}{\Delta t} \quad (3.6)$$

Finally Δt can be made very small and Eq. 3.4 reduces to

$$\text{Accumulation} = V \frac{dc}{dt} \quad (3.7)$$

Thus mass accumulates as concentration increases with time (positive dc/dt) and diminishes as concentration decreases with time (negative dc/dt). For the steady-state case, mass remains constant ($dc/dt = 0$). Note that the units of accumulation (as with all other terms in the balance) are mass per time ($M T^{-1}$).

Loading. Mass enters a lake from a variety of sources and in a number of different ways. For example mass carried by treatment plant effluents and tributary streams enters a lake at a point on its periphery. In contrast atmospheric sources, such as precipitation and dry fallout, are introduced in a distributed fashion across the air-water interface at the lake's surface. Whereas the position and manner of entry of loadings would have fundamental importance for incompletely mixed water bodies such as streams and estuaries, it is unimportant for our completely mixed system. This is because, by definition, all inputs are instantaneously distributed throughout the volume. Thus, for the present case, we lump all loadings into a single term, as in

$$\text{Loading} = W(t) \quad (3.8)$$

where $W(t)$ = rate of mass loading ($M T^{-1}$) and (t) signifies that loading is a function of time.

It should be noted that in a later part of this lecture we formulate loading in a slightly different fashion than in Eq. 3.8. Rather than as a single value $W(t)$, we will represent it as the product (recall Eq. 1.3)

$$\text{Loading} = Qc_{in}(t) \quad (3.9)$$

where Q = volumetric flow rate of all water sources entering the system ($L^3 T^{-1}$) and $c_{in}(t)$ = average inflow concentration of these sources ($M L^{-3}$). Note that we have assumed that Q is constant and that all the temporal variations in loading are the result of temporal variations in the inflow concentration. Also recognize that average inflow concentration can be related to loading by equating Eqs. 3.8 and 3.9 and solving for

$$c_{in}(t) = \frac{W(t)}{Q} \quad (3.10)$$

Outflow. In our simple system (Fig. 3.1) mass is carried from the system by an outflow stream. The rate of mass transport can be quantified as the product of the volumetric flow rate Q and the outflow concentration c_{out} ($M L^{-3}$). But, because of our well-mixed assumption, the outflow concentration by definition equals the in-lake concentration $c_{out} = c$, and the outflow sink can be represented by

Reaction. Although there are many different ways to formulate reactions that purge pollutants from natural waters, the most common by far is a first-order representation (recall Eq. 2.10)

$$\text{Reaction} = kM \tag{3.12}$$

where k = a first-order reaction coefficient (T^{-1}). Thus a linear proportionality is assumed between the rate at which the pollutant is purged and the mass of pollutant that is present. Equation 3.12 can be expressed in terms of concentration by substituting Eq. 3.4 into Eq. 3.12 to yield

$$\text{Reaction} = kVc \tag{3.13}$$

Settling. Settling losses can be formulated as a flux of mass across the surface area of the sediment-water interface (Fig. 3.2). Thus by multiplying the flux times area, a term for settling in the mass balance can be developed as

$$\text{Settling} = vA_s c \tag{3.14}$$

where v = apparent settling velocity ($L T^{-1}$) and A_s = surface area of the sediments (L^2). The settling velocity is called "apparent" because it represents the net effect of the various processes that act to deliver pollutant to the lake's sediments.

example some of the pollutant may be in dissolved form and hence not subject to settling. For such cases a "real" settling velocity cannot be used to represent the net effect of this mechanism.

Because volume is equal to the product of mean depth H and lake surface area A_s , Eq. 3.14 can also be formulated in a fashion similar to the first-order reaction, as in

$$\text{Settling} = k_s Vc \tag{3.15}$$

where k_s = a first-order settling rate constant = v/H . Notice that the ratio v/H has the same units (T^{-1}) as the reaction rate k . The validity of this representation is contingent on the assumption that the lake's surface area and the sediment area are

The format of Eq. 3.14 is preferable to Eq. 3.15 because the former faithfully captures the mechanistic nature of settling, that is, as a mass transfer a surface (see Box 3.1).

Total balance. The terms can now be combined into the following mass balance for a well-mixed lake:

$$V \frac{dc}{dt} = W(t) - Qc - kVc - vA_s c \tag{3.16}$$

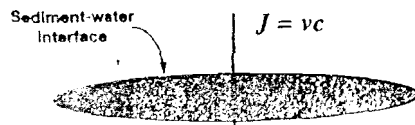


FIGURE 3.2 Settling losses formulated as a flux of mass

Before proceeding to solutions for Eq. 3.16 we should introduce some nomenclature. Concentration c and time t are the *dependent* and the *independent variables*, respectively, because the model is designed to predict concentration as a function of time. The loading term $W(t)$ is referred to as the model's *forcing function* because it represents the way in which the external world influences or "forces" the system. Finally the quantities V , Q , k , v , and A_s are referred to as *parameters* or coefficients. Specification of these parameters will allow us to apply our model to particular lakes and pollutants.

BOX 3.1. Parameterization

As described in this section, settling losses can be parameterized as the product of settling velocity, surface area, and concentration $vA_s c$. However, as in Eq. 3.15, the settling mechanism can also be "parameterized" as a first-order rate. This is done by multiplying the settling-velocity version by H/H and collecting terms to yield

$$vA_s c \frac{H}{H} = \frac{v}{H} (AH)c = k_s Vc$$

where k_s = a settling first-order rate constant (T^{-1}) that is equal to

$$k_s = \frac{v}{H}$$

This alternative formulation has been commonly employed in water-quality modeling.

Now the question arises, is either way superior? From a strictly mathematical standpoint they are identical. However, because it is more fundamental, the settling velocity parameterization is superior. By fundamental I mean that it more directly represents the process being modeled. That is, each term in $vA_s c$ represents a characteristic of the process that can be measured independently. In contrast the k_s term confounds two independent properties: settling and depth.

Why is this a problem? First, the k_s version is system specific (because it implicitly includes a system-specific property, mean depth) and hence is awkward to extrapolate to other systems. If we measure a k_s in a particular system, we could use it only in other systems of the same depth. Thus, to extrapolate to a system with a different depth, we would have to revert to the settling velocity format anyway. Second, what if depth is changing? For this case the use of k_s clearly breaks down.

Now, where might confounding parameters be advantageous? For one thing, within a mathematical calculation for a particular system, we often find it useful to collect terms for mathematical convenience. Second, it is often of use to collect terms so that processes can be compared in commensurate units. For example the relative magnitudes of settling and a reaction could be assessed by comparing v/H versus k . Finally there are some instances where we might confound several parameters because one or more do not vary between systems and/or they are difficult to measure.

Throughout the remainder of this book the issue of proper parameterization will continuously arise as we attempt to quantify the processes observed in natural waters. When it arises we will discuss its further nuances.

3.2 STEADY-STATE SOLUTIONS

If the system is subject to a constant loading W for a sufficient time, it will attain a dynamic equilibrium condition called a *steady-state*. In mathematical terms this means that accumulation is zero (that is, $dc/dt = 0$). For this case Eq. 3.16 can be solved for

$$c = \frac{W}{Q + kV + vA_s} \quad (3.17)$$

or using the format of Eq. 1.8,

$$c = \frac{1}{a} W \quad (3.18)$$

where the assimilation factor is defined as

$$a = Q + kV + vA_s, \quad (3.19)$$

The steady-state solution provides our first illustration of the benefits of the mechanistic approach. That is, it has successfully yielded a formula that defines the assimilation factor in terms of measurable variables that reflect the system's physics, chemistry, and biology.

EXAMPLE 3.1. MASS BALANCE. A lake has the following characteristics:

- Volume = 50,000 m³
- Mean depth = 2 m
- Inflow = outflow = 7500 m³ d⁻¹
- Temperature = 25°C

The lake receives the input of a pollutant from three sources: a factory discharge of 50 kg d⁻¹, a flux from the atmosphere of 0.6 g m⁻² d⁻¹, and the inflow stream that has a concentration of 10 mg L⁻¹. If the pollutant decays at the rate of 0.25 d⁻¹ at 20°C ($\theta = 1.05$),

- (a) Compute the assimilation factor.
- (b) Determine the steady-state concentration.
- (c) Calculate the mass per time for each term in the mass balance and display your results on a plot.

Solution: (a) The decay rate must first be corrected for temperature (Eq. 2.44):

$$k = 0.25 \times 1.05^{25-20} = 0.319 \text{ d}^{-1}$$

Then the assimilation factor can be calculated as

$$a = Q + kV = 7500 + 0.319(50,000) = 23,454 \text{ m}^3 \text{ d}^{-1}$$

Notice, how the units look like flow (that is, volume per time). This is because the same mass units are used in the numerator and the denominator and they cancel, as in

(b) The surface area of the lake is needed to calculate the atmospheric loading

$$A_s = \frac{V}{H} = \frac{50,000}{2} = 25,000 \text{ m}^2$$

The atmospheric load is then computed as

$$W_{\text{atmosphere}} = JA_s = 0.6(25,000) = 15,000 \text{ g d}^{-1}$$

The load from the inflow stream can be calculated as

$$W_{\text{inflow}} = 7500(10) = 75,000 \text{ g d}^{-1}$$

Therefore the total loading is

$$W = W_{\text{factory}} + W_{\text{atmosphere}} + W_{\text{inflow}} = 50,000 + 15,000 + 75,000 = 140,000 \text{ g d}^{-1}$$

and the concentration can be determined as (Eq. 3.18)

$$c = \frac{1}{a} W = \frac{1}{23,454} 140,000 = 5.97 \text{ mg L}^{-1}$$

(c) The loss due to flushing through the outlet can be computed as

$$Qc = 7500(5.97) = 44,775 \text{ g d}^{-1}$$

and the loss due to reaction as

$$kVc = 0.319(50,000)5.97 = 95,225 \text{ g d}^{-1}$$

These results along with the loading can be displayed as in Fig. 3.3.

The representation in Fig. 3.3 can now be related back to the parable of the blind men and the elephant. Each arrow, representing a source or sink mechanism, is analogous to the individual parts of the elephant. It is only when they are tied

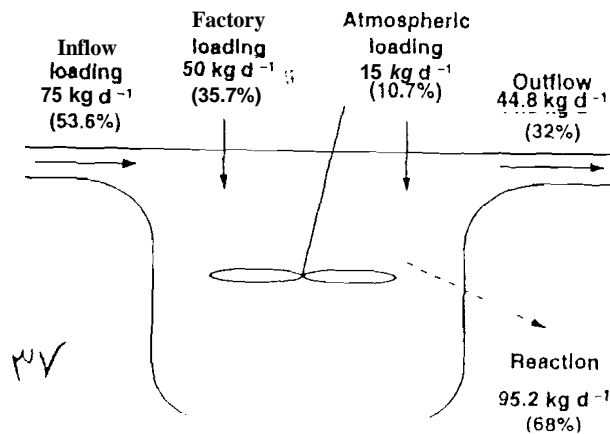


FIGURE 3.3

A mass balance for the well-mixed lake from Example 3.1. The arrows represent the major sources and sinks of the pollutant. The mass-transfer rates have also been included along with the percent of total mass. Inflow accounted for by

together by the mass balance that we can assess their combined effect. Thus the model provides an integrated view of the system.

BOX 3.2. "Stream-of Consciousness" Versus "Cartoon" Modeling

"Stream of consciousness" is a psychological term, coined by the psychologist William James, that characterizes individual conscious experience as a succession of states constantly moving onward in time. The idea has been transferred to literature in the form of "stream-of-consciousness" writing. In its finest expression an individual's interior monologue is used to reveal character and comment on life. At its worst it amounts to a self-indulgent mind dump.

Unfortunately many creative exercises can be approached in the latter fashion. For example computer programs are often written without prior thought. Individuals sit down at a computer console and just begin typing. Invariably the final result (as well as the ultimate time investment) suffers from the haphazard approach and lack of design.

Mathematical models can also be developed in a stream-of-consciousness fashion. There is often the tendency to start writing mass balances without adequate forethought. As expected, the results are often incorrect or incomplete. In the best case a correct model results only after many time-consuming revisions.

Some simple steps can be applied to avoid such pitfalls:

- *Draw a diagram.* For the simple well-mixed models described up to now, this merely consists of sketching the major sources and sinks of the pollutant being modeled. Although this might seem trivial, the act of drawing forces you to delineate the mechanisms governing pollutant dynamics. In later lectures, as we deal with multiple pollutants in segmented systems, diagrams will become essential. Dr. Bob Broshears of the U.S. Geological Survey calls this "cartoon modeling." Although this terminology might sound flippant, it is not meant to be. Experienced modelers recognize that a well-thought-out schematic is critical to keeping track of all the variables and processes in a complicated model.
- *Write equations.* After a schematic is developed, it can be translated into model equations. For the simple case discussed so far, each arrow represents a term in the mass balance. In later lectures, there will be many variables (boxes) connected by many processes (arrows). Thus the schematic provides a guide for ensuring that the mathematical characterization is complete.
- *Obtain a solution.* This can be accomplished exactly (algebra or calculus) or approximately (numerical methods). For more complicated systems, computers are necessary.
- *Check results.* This last step is sometimes neglected by the novice modeler. Too many people trust model output if it "looks reasonable." Unfortunately this tendency increases when computers are involved. And if the results are displayed in high-resolution graphics in multiple colors, certain individuals lose any vestige of skepticism. Therefore, whether checking a homework solution or a large professional code, sufficient testing is required to ensure that the model is producing correct results. Beyond obvious and easily recognizable bloopers (e.g., a negative concentration), the simplest starting point is to check that mass is conserved. Beyond that, more complex issues will be touched on these when I review model development.

3.2.1 Transfer Functions and Residence Time

Aside from the assimilation factor, there are a variety of other ways to summarize the ability of a steady-state system to assimilate pollutants.

Transfer function. An alternative way to formulate Eq. 3.17 is based on expressing the loading in the format of Eq. 3.9. For the steady-state case this is

$$W = Qc_{in} \quad (3.20)$$

Equation 3.20 can be substituted into Eq. 3.17, and both the numerator and denominator of the result can be divided by c_{in} to yield

$$\frac{c}{c_{in}} = \beta \quad (3.21)$$

where β = the transfer function

$$\beta = \frac{Q}{Q + kV + vA_s} \quad (3.22)$$

Equation 3.22 is called a **transfer function**† because it specifies how the system input (as represented by c_{in}) is transformed or "transferred" to an output (as represented by c). Examination of Eq. 3.22 provides insight into how the model "works." If $\beta \ll 1$, then the lake's removal mechanisms will act to greatly reduce the level of pollutant in the lake; that is, such a lake has great assimilative capacity. Conversely if $\beta \rightarrow 1$, then the lake's removal mechanisms (the denominator) are weak relative to its supply mechanism (the numerator). For such cases the pollutant level will approach that of the inflow. In other words the lake's assimilative capacity is minimal.

Thus the lake's assimilative capacity can be evaluated by the dimensionless number β . Inspection of Eq. 3.22 indicates that for the simple model in Fig. 3.1, assimilation increases for large values of reaction rate, settling velocity, volume, and area. Note that flow which appears in both the numerator and the denominator acts to both increase and decrease assimilation. It increases assimilation as it reflects rushing of pollutant through the lake's outlet. It decreases assimilation as it reflects delivery of pollutant through the lake's inflow.

Residence time. The residence time τ_E of a substance E represents the mean amount of time that a molecule or particle of E would stay or "reside" in a system. It is defined for a steady-state, constant-volume system as (Stumm and Morgan 1981)

$$\tau_E = \frac{E}{|dE/dt|_z} \quad (3.23)$$

where E = quantity of E in the volume (either M or ML^{-3}) and $|dE/dt|_z$ = absolute value of either the sources or the sinks (either MT^{-1} or $ML^{-3}T^{-1}$).

One of the simpler applications of Eq. 3.23 is the determination of the residence time of water in a lake. Since the density of water is by definition approximately 1 g cm^3 , the quantity of water in a lake is equivalent to its volume. In a similar

sense the "sink" of water from a lake is measured by the magnitude of its outflow (assuming that evaporation = precipitation). Substituting these values into Eq. 3.23 yields the water residence time

$$\tau_w = \frac{V}{Q} \quad (3.24)$$

This relationship is useful for understanding the general notion of residence time since it has a straightforward physical interpretation—it is the amount of time that would be required for the outflow to replace the quantity of water in the lake. Thus it is a measure of the lake's flushing rate. If the volume is large and the flow is small the lake has a long residence time; that is, it is a slow flusher. Conversely lakes with short residence times (high flow and small volume) are referred to as fast flushers.

Equation 3.23 can also be used to compute a "pollutant residence time." For example for the system in Fig. 3.1, the sinks can be represented on a mass basis by

$$\left. \frac{dM}{dt} \right|_z = Qc + kVc + vA_s c \quad (3.25)$$

This equation, along with Eq. 3.4, can be substituted into Eq. 3.23 to give

$$\tau_c = \frac{V}{Q + kV + vA_s} \quad (3.26)$$

Note that Eqs. 3.24 and 3.26 are similar in form with the exception that the pollutant residence time is affected by reactions and settling in addition to the outflow.

EXAMPLE 3.2. TRANSFER FUNCTION AND RESIDENCE TIMES. For the lake in Example 3.1, determine the (a) inflow concentration, (b) transfer function, (c) water residence time, and (d) pollutant residence time.

Solution: (a) The inflow concentration is computed as

$$c_{in} = \frac{W}{Q} = \frac{140,000}{7500} = 18.67 \text{ mg L}^{-1}$$

(b) The transfer coefficient can now be determined as

$$\beta = \frac{c}{c_{in}} = \frac{Q}{Q + kV} = 0.32$$

Thus the removal processes act to create a lake concentration that is 32% of the inflow concentration.

(c) The residence time can be calculated as

$$\tau_w = \frac{V}{Q} = \frac{50,000}{7500} = 6.67 \text{ d}$$

(d) The pollutant residence time is

$$\tau_c = \frac{V}{Q + kV} = \frac{50,000}{7500 + 0.319(50,000)} = 2.13 \text{ d}$$

Because of the addition of the decay term, the residence time of a pollutant is about one-third the water residence time.

BOX 3.3. Estimating Reaction Kinetics with a Steady-State CSTR

Grady and Lim (1980) describe a method for evaluating reaction kinetics using experiments conducted with CSTRs. In this approach, which they call the *algebraic method*, the reactors are run to a steady-state. At this point the mass balance can be written as

$$Qc_{in} - Qc - rV = 0 \quad (3.27)$$

where r = rate of consumption of the reactant ($\text{M L}^{-3} \text{T}^{-1}$). If all the other quantities are measured the balance can be solved for the consumption rate

$$r = \frac{Qc_{in} - Qc}{V} = \frac{1}{\tau_w} (c_{in} - c) \quad (3.28)$$

If we assume that Eq. 2.7 holds,

$$r = kc^n \quad (3.29)$$

The parameters k and n can be determined by taking the natural logarithm,

$$\ln r = \ln k + n \ln c \quad (3.30)$$

Thus if a plot of $\ln r$ versus $\ln c$ yields a straight line, Eq. 2.7 holds, and the slope and intercept can be used to calculate k and n . An exercise on the approach is presented in Prob. 3.5 at the end of this lecture.

3.3 TEMPORAL ASPECTS OF POLLUTANT REDUCTION

To this point we have focused on steady-state solutions. These provide an estimate of the average water quality that will result if loadings are held constant for a sufficiently long time period. In addition to steady-state predictions, water-quality managers are also interested in the temporal response of natural waters.

Suppose that a system is at steady-state. At a specific time a waste removal project is implemented. As depicted in Fig. 3.4, two interrelated questions arise:

- How long will it take for improved water quality to occur?
- What will the "shape" of the recovery look like?

To determine the correct trajectory, let's start with the mass-balance model (Eq. 3.16)

$$V \frac{dc}{dt} = W(t) - Qc - kVc - vA_s c \quad (3.31)$$

Before solving this equation, we can divide it by volume to yield

$$\frac{dc}{dt} = \frac{W(t)}{V} - \frac{Q}{V}c - kc - \frac{v}{H}c \quad (3.32)$$

Collecting terms gives

$$\frac{dc}{dt} + \lambda c = \frac{W(t)}{V} \quad (3.33)$$

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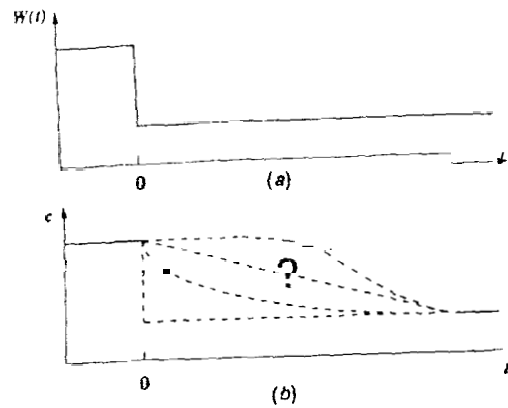


FIGURE 3.4 (a) A waste load reduction along with (b) four possible recovery scenarios for concentration.

where

$$\lambda = \frac{Q}{V} + k + \frac{v}{H} \quad (3.34)$$

in which λ is called an *eigenvalue* (that is, a characteristic value).

If all the parameters (Q, V, k, v, H) are constant, Eq. 3.33 is a nonhomogeneous, linear, first-order, ordinary differential equation. Its solution consists of two parts,

$$c = c_g + c_p \quad (3.35)$$

where c_g = general solution for the case $W(t) = 0$ and c_p = particular solution specific forms of $W(t)$.

Because the general solution corresponds to the case where the loading is terminated, it is ideal for investigating a system's recovery time. As described next it will also provide us with insight into the shape of the recovery.

3.3.1 The General Solution

If $c = c_0$ at $t = 0$, Eq. 3.33 with $W(t) = 0$ can be solved by the separation of variables (recall solution of Eq. 2.10):

$$c = \quad (3.36)$$

Thus we have arrived at an equation that describes how the lake's concentration changes as a function of time following the termination of waste loading.

The behavior of Eq. 3.36 is clearly dictated by the exponential function as in Fig. 3.5, for the case where the argument of the function (that is, the value to which e is raised: x) is zero, the exponential function's value is unity. Thereafter if the argument is positive, the function increases in an accelerated fashion; that is, it doubles its value at set intervals of $x (= 0.693)$. In contrast if the argument is negative, the function asymptotically decreases toward zero by halving at the set intervals.

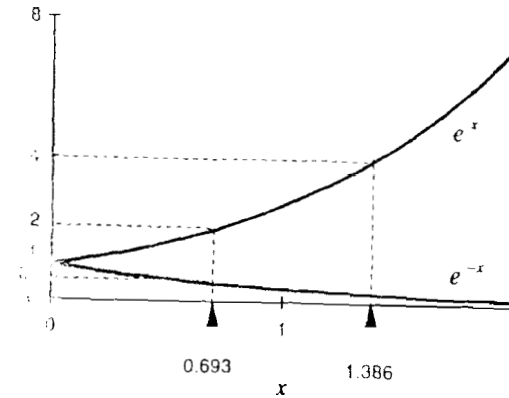


FIGURE 3.5 The exponential function

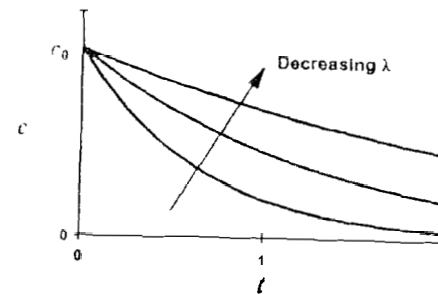


FIGURE 3.6 The temporal response of our well-mixed lake model following the termination of all loadings at $t = 0$.

Thus we can now interpret Eq. 3.36. As in Fig. 3.6 the negative value of the argument means that the concentration decreases and asymptotically approaches zero. Further the rate of decrease is dictated by the magnitude of the eigenvalue λ . If λ is large, the lake's concentration will decrease rapidly. If λ is small, the lake's response will be slow.

EXAMPLE 3.3. GENERAL SOLUTION. In Example 3.1 we determined the steady-state concentration for a lake having the following characteristics:

- Volume = 50,000 m³
- Mean depth = 2 m
- Inflow = outflow = 7500 m³ d⁻¹
- Temperature = 25°C
- Waste loading = 140,000 g d⁻¹
- Decay rate = 0.319 d⁻¹

If the initial concentration is equal to the steady-state level (5.97 mg L⁻¹), determine the general solution.

Solution: The eigenvalue can be computed

$$\lambda = \frac{Q}{V} + k = \frac{7500}{50,000} + 0.319 = 0.469 \text{ d}^{-1}$$

Thus the general solution is

$$c = 5.97e^{-0.469t}$$

which can be displayed graphically as

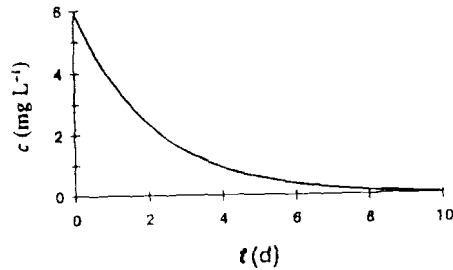


FIGURE E3.3

Note that by $t \approx 5$ d the concentration is reduced to less than 10% of its original value. By $t = 10$ d, for all intents and purposes, it has reached zero.

An interesting property of the general solution is that even though the loading is reduced to zero, the concentration will never reach zero. This introduces an element of ambiguity into the analysis. We now attempt to resolve this ambiguity by introducing the concept of response time.

3.3.2 Response Time

Although the parameter group A clearly dictates the lake's temporal response characteristics, it has shortcomings for communicating with decision makers. First, it has the counterintuitive property that as it gets large the time for the lake to respond gets small. Second, as mentioned in the previous section, its interpretation is clouded by the fact that, from a strictly mathematical perspective, the underlying cleansing process never reaches completion. Try telling a politician that a cleanup would theoretically take forever! They tend to react very unfavorably to asymptotic solutions that extend beyond the next election.

Both these shortcomings can be rectified by using the general solution to derive a new parameter group. Called the *response time*, this parameter group represents the time it takes for the lake to complete a fixed percentage of its recovery. Thus the problem of ambiguity is remedied by deciding "how much" of the recovery is judged as being "enough." For example we might assume that if the lake has experienced 95% of its recovery we would be satisfied that, for all practical purposes, the remedial measure is successful.

In terms of Eq. 3.36 a 50% response time means that the concentration is lowered to 50% of its initial value, or

$$0.50c_0 = c_0 e^{-\lambda t_{50}} \quad (3.37)$$

where $t_{50} = 50\%$ response time (T). Dividing by the exponential and $0.50c_0$ yields

$$e^{\lambda t_{50}} = 2 \quad (3.38)$$

TABLE 3.1
Response times

Response time	t_{50}	$t_{63.2}$	t_{75}	t_{90}	t_{95}	t_{99}
Formula	$0.693/\lambda$	$1/\lambda$	$1.39/\lambda$	$2.3/\lambda$	$3/\lambda$	$4.6/\lambda$

Taking the natural logarithm and solving for t_{50} gives

$$t_{50} = \frac{0.693}{\lambda} \quad (3.39)$$

Thus we can see that the 0.693 we observed previously (recall discussion of Fig. 3.5) is actually the natural logarithm of 2. Note that the quantity t_{50} is also commonly referred to as a half-life (recall Sec. 2.2.4).

The above derivation can be generalized to compute an arbitrary response time by the formula

$$t_{\phi} = \frac{1}{\lambda} \ln \frac{100}{100 - \phi} \quad (3.40)$$

where $t_{\phi} = \phi\%$ response time. For example if we are interested in determining how long it takes to reach 95% of its ultimate recovered level, we could compute

$$t_{95} = \frac{1}{\lambda} \ln \frac{100}{100 - 95} = \frac{3}{\lambda} \quad (3.41)$$

Table 3.1 and Fig. 3.7 show other response times. As would be expected, the higher the percentage of recovery, the longer the response time.

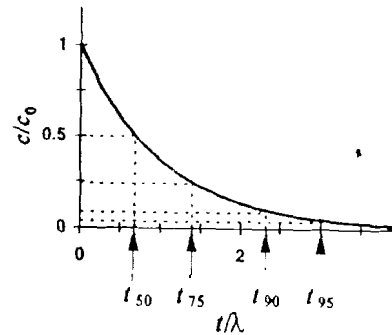


FIGURE 3.7
A plot of the general solution showing values of several response times

EXAMPLE 3.4. RESPONSE TIME. Determine the 75%, 90%, 95%, and 99% response times for the lake in Example 3.3.

Solution: The 75% response time can be computed as

$$t_{75} = \frac{1.39}{0.469} = 2.96 \text{ d}$$

In a similar fashion we can compute $t_{90} = 3.9$ d, $t_{95} = 6.4$ d, and $t_{99} = 9.8$ d

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As in Example 3.4 there is a certain amount of subjectivity involved in deciding "how much" of the recovery is judged as being "enough." In general I recommend using either t_{90} or t_{95} . They are neither too lenient nor too stringent and conform to what most individuals would deem an acceptable level of recovery.

BOX 3.4. The Rule of 72

Before the days of handheld calculators and computers, bankers and financiers needed a quick way to evaluate their investments. To do this they developed a heuristic that is called *the rule of 72*. According to the rule, the time required to double your money can be estimated as

$$\text{Doubling time} \cong \frac{72}{\text{interest rate (\%)}}$$

For example if you invested some money at an annual interest rate of 6%, it would double in approximately 12 years. The same formula can also be employed to assess how the value of your money decreases due to inflation. For example if the inflation rate is 3%, the money hidden in your mattress would lose half its value in 24 years.

This formula is derived from the concept of the half-life. In fact a more accurate representation, based on Eq. 3.41, might be called "the rule of 69.3,"

$$\text{Doubling time} = \frac{69.3}{\text{interest rate (\%)}}$$

The reason that a numerator of 72 was chosen is that it is more easily divided by whole number interest rates. For example

$$\begin{array}{lll} 72/1 = 72 \text{ yr} & 72/5 \cong 14 \text{ yr} & 72/9 = 8 \text{ yr} \\ 72/2 = 36 \text{ yr} & 72/6 = 12 \text{ yr} & 72/10 \cong 7 \text{ yr} \\ 72/3 = 24 \text{ yr} & 72/7 \cong 10 \text{ yr} & \\ 72/4 = 18 \text{ yr} & 72/8 = 9 \text{ yr} & \end{array}$$

Thus you can quickly figure the time required to double or halve your money. Aside from providing you with a handy means for evaluating your investments, we have included this discussion to illustrate how first-order processes and compound interest are based on similar mathematics.

PROBLEMS

3.1. A pond with a single inflow stream has the following characteristics:

$$\begin{array}{l} \text{Mean depth} = 3 \text{ m} \\ \text{Surface area} = 2 \times 10^5 \text{ m}^2 \\ \text{Residence time} = 2 \text{ weeks} \\ \text{Inflow BOD concentration} = 4 \text{ mg L}^{-1} \end{array}$$

A subdivision housing 1000 people will discharge raw sewage into this system. Each individual contributes about $150 \text{ gal capita}^{-1} \text{ d}^{-1}$ of wastewater and $0.25 \text{ lb capita}^{-1} \text{ d}^{-1}$ of biochemical oxygen demand (BOD).

- Determine the BCD concentration of the wastewater in mg L^{-1} .
- If the BOD decays at a rate of 0.1 d^{-1} and settles at a rate of 0.1 m d^{-1} , calculate the assimilation factor for the pond prior to building the subdivision. Which of the purging mechanisms are most effective? List them in decreasing order of effectiveness.
- Calculate the transfer function factor after building the subdivision.
- Determine the steady-state concentration for the lake with and without the subdivision.

3.2. A lake with a single inflow stream has the following characteristics:

$$\begin{array}{l} \text{Mean depth} = 5 \text{ m} \\ \text{Surface area} = 11 \times 10^6 \text{ m}^2 \\ \text{Residence time} = 4.6 \text{ yr} \end{array}$$

An industrial plant presently discharges malathion ($W = 2000 \times 10^6 \text{ g yr}^{-1}$) to the lake. In addition the inflowing stream also contains malathion ($c_{in} = 15 \text{ mg L}^{-1}$). Note that the volumetric rate of inflow and outflow are equal. Assuming that a first-order decay reaction can be used to characterize malathion decay ($k = 0.1 \text{ yr}^{-1}$),

- Write a mass-balance equation for malathion for this system.
 - If the lake is at steady-state, compute the in-lake malathion concentration.
 - If the lake is at steady-state, what industrial plant loading rate must be maintained to lower the lake's concentration to 30 ppm? Express your result as a percent reduction.
 - Evaluate each of the following engineering options to determine which is the most effective for lowering the steady-state concentration:
 - Reduce the present loading rate of the industrial plant by building a waste treatment facility that will remove 50% of the malathion from the plant's effluent.
 - Double the lake's depth by dredging.
 - Double the lake's outflow rate Q by diverting malathion-free water from a nearby unpolluted stream into the lake.
 - What other factors would need to be considered (aside from lowering concentration) when making a decision in (d) in the "real world"?
 - Determine the 95% response times for each of the options in part (d).
- 3.3. Recall from Example 1.3 that in the early 1970s Lake Ontario had a total phosphorus loading of approximately 10,500 mta (metric tons per annum) and an in-lake concentration of $21 \mu\text{g L}^{-1}$ (Chapra and Sonzogni 1979). It is known that the only losses of total phosphorus for the lake are settling and flushing through the lake's outlet. Assume the outflow rate is $212 \text{ km}^3 \text{ yr}^{-1}$ and the sediment area is $10,500 \text{ km}^2$.
- Calculate the inflow concentration for the system. Assume that water inflow equals outflow.
 - Use a mass balance to estimate the apparent settling velocity for total phosphorus in this lake.

3.4. A lake has the following characteristics:

$$\begin{array}{l} \text{Volume} = 11 \times 10^6 \text{ m}^3 \\ \text{Surface Area} = 1 \times 10^5 \text{ m}^2 \\ \text{Water residence time} = 0.3 \text{ yr} \end{array}$$

A soluble pesticide is input to the lake at a rate of $10 \times 10^6 \text{ mg yr}^{-1}$. The in-lake concentration is $0.8 \mu\text{g L}^{-1}$.

- Determine the inflow concentration (assume inflow = outflow).
- Determine the transfer function.
- If the only removal mechanism (other than flushing) is volatilization, compute the flux of the pesticide out the lake's surface and to the atmosphere.
- Express the result of part (c) as a volatilization velocity.

- 3.5.** A rate experiment is performed for a 1-L CSTR. The inflowing concentration is held steady at a level of 100 mg L^{-1} . The flow is varied and the resulting outflow concentrations are measured:

$Q \text{ (L hr}^{-1}\text{)}$	0.1	0.2	0.4	0.8	1.6
$c \text{ (mg L}^{-1}\text{)}$	23	31	41	52	64

Use the algebraic method to determine the rate and order of the reaction.

- 3.6.** Derive Eq. 3.40.

- 3.7.** A pond with a single inflow stream has the following characteristics:

Mean depth = 3 m
 Surface area = $2 \times 10^5 \text{ m}^2$
 Residence time = 2 wk

A subdivision will discharge raw sewage into this system. If BOD decays at a rate of 0.1 d^{-1} and settles at a rate of 0.1 m d^{-1} , calculate the 75%, 90%, and 95% response times for the pond.

- 3.8.** Determine a half-life for a batch reactor with a second-order decay reaction.

- 3.9.** Compute the first-order reaction rates for the following substances:

- cesium-137 (half-life = 30 yr)
- iodine-131 (half-life = 8 d)
- tritium (half-life = 12.26 yr)

- 3.10.** A lake (volume = $10 \times 10^6 \text{ m}^3$, water residence time = 2 months) is located adjacent to a railway line that carries considerable traffic of chemicals. You are hired as a consultant to provide insight into potential spills into the lake. If the lake is assumed to be completely mixed, a spill would be distributed instantaneously throughout the volume. Therefore the resulting concentration would be $c_0 = m/V$, where m is the mass of pollutant that is spilled. Thereafter the lake's response would follow the general solution.
- Develop a plot of t_{75} , t_{95} , and t_{99} versus pollutant half life. Use logarithmic scales where you believe they would be helpful.
 - Include a short "user's manual" for the plot to provide managers with guidance for its use and interpretation.